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Preparation of porous nanoparticle TiO_2 films for flexible dye-sensitized solar cells

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A TiO_2 paste was prepared by mixing commercial TiO_2 (P25), ethanol, distilled water and a small amount of Ti (IV) tetraisopropoxide (TTIP), following by a hydrothermal treatment. Before hydrothermal treatment, a stirring for 48 h can prevent cracking TiO_2 films. TTIP significantly promote the chemical connection between TiO_2 particles and its adherence to the substrate, the TTIP amount of 6 mol% is suitable. UV irradiation can remove some impurities and water from the TiO_2 film with an optimal time of 2 h. Transmission electron microscopy, X-ray diffraction, scanning electron microscopy and photovoltaic tests are characterized and measured. Short-circuit current density, open-circuit voltage, fill factor and photoelectric conversion efficiencies for the fabricated flexible dye-sensitized solar cell are 7.20 mA cm^{-2}, 0.769 V, 0.686 and 3.84%, respectively, under irradiation with a simulated solar light of 100 mW cm^{-2}.

flexible DSSC, TiO_2 film, TTIP, UV treatment

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Since the prototype of dye-sensitized solar cell (DSSC) was first reported in 1991, it has received widely interest because of its low cost and simple preparation, and DSSCs with photoelectric conversion efficiencies of 11% have been achieved [1,2]. DSSC consists of a conducting substrate, nano-porous oxide film, dye sensitizer, electrolyte and counter electrode. The conducting substrate usually is made of a transparent conductive glass, which limit DSSCs practical applications because of its weight, frangibility and high cost. DSSCs based on flexible substrate have attracted wide interest due to its merits, such as light weight, good flexibility, impact-proof, lower cost [3,4]. Besides, their shapes or surfaces can be devised and constructed, the technique of large-scale continuous production and rapid coating can be used, which further decrease the production cost [3–6].

The conventional method for obtaining an efficient electrode materials is the high-temperature calcination of nanocrystalline semiconductor particles. Colloidal pastes containing organic additives are often used, with the latter essential to suppress particle agglomeration and reduce stress during calcination. Crack-free well-adhered films with optimal mesoporous structure can then be obtained. High-temperature annealing (> 400°C) can remove organic additives and promote chemical interconnection between particles to establish an electrical connection [7]. The requirement of high temperature clearly excludes using plastic-film substrates, and the development of low-temperature methods is necessary for the realization of flexible DSSCs. The current performance of such films is much lower than those prepared conventionally as above. The low-temperature preparation of TiO_2 films can result in incomplete interconnection with adjacent particles and poor adherence of the film to the substrate. Much efforts have been devoted to overcome the problems associated with preparing porous

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TiO_2 films at low-temperatures [8–12]. Zhang et al. [8] obtained a flexible DSSC with photoelectric conversion efficiency of 3.27%, Uchida et al. [9] and Hart et al. [10] reported flexible DSSC with photoelectric conversion efficiency of 2.16% and 2.44%, Yang et al. [11] reported flexible DSSC with photoelectric conversion efficiency of 5.7% and we achieved a flexible DSSC with photoelectric conversion efficiency 3.4% [12].

In this paper, a TiO_2 slurry was prepared by hydrothermal treating mixture of commercial TiO_2 (P25), Ti (IV) tetraisopropoxide (TTIP), ethanol and distilled water in an autoclave. A flexible photoanode was fabricated by scraping the TiO_2 slurry on ITO coated poly(ethylene naphthalate) substrate at low-temperature. Using Pt-coated ITO/PEN as counter electrode, the dye N719 as sensitizer, and the redox electrolyte consisted of tetrabutyl ammonium iodide, LiI, I_2, 4-tert-butyl-pyridine and acetonitrile, a flexible DSSC was assembled and its photoelectric conversion efficiency was 3.84% under irradiation with a simulate solar light intensity of 100 mW/cm^2 .

1 Materials and methods

1.1 Materials

Ethanol, iodine, lithium iodide, tetrabutyl ammonium iodide, acetonitrile (AN) sodium hydroxide and 4-tert-butyl-pyridine (TBP) were purchased from the Shanghai Chemical Agency Ltd., China (Analysis purity grade). Ti (IV) tetraisopropoxide (95%) was obtained from Aldrich Co. Sensitized-dye N719 [cis-di(thiocyanato)-N,N'-*bis*(2,2′-bi-pyridyl-4-carboxylicacid-4-tetrabutylammonium carboxylate) ruthenium(II)] was obtained from Solaronix SA, Switzerland. TiO_2 nanoparticles (P25) were obtained from Degussa, Germany. All above agents were used without further purification. ITO/PEN (12 Ω/cm^2) and Pt-ITO/PEN (5 Ω/cm^2) polymer substrates were purchased from the Peccell Technologies of Japan.

1.2 Nanocrystalline TiO_2 film preparation

TiO_2 (P25) powder was pretreated [8] at 450°C for 30 min in an Electric Muffle Furnace (Shanghai, China), then cooled to room temperature. A mixture of treated TiO_2, distilled water and absolute ethanol of molar ratio 1∶1∶5 was stirred at room temperature. Small quantities of Ti (IV) tetraisopropoxide were added to the above TiO_2 paste, to give molar percentages of 0, 2%, 4%, 6%, 8% and 10%. After adequately stirring, paste mixtures were hydrothermally treated in an autoclave (packing volume < 80%) at 185°C for 12 h, from which 6 paste samples were obtained.

ITO/PEN substrate was dipped in a 50% ethanol solution for 24 h without ultrasonic oscillation, then the substrate was cleaned with 95% ethanol repeated for several times. The cleaned substrate was kept in absolute ethanol. The substrate was blow dried prior to using. The TiO_2 colloid was coated onto the ITO/PEN substrate by a doctor-blading technique. The process was repeated for three times to form a thick TiO_2 film. The thickness of the TiO_2 nanocrystalline film was controlled by the thickness of adhesive tape around the edge of the cleaned ITO/PEN substrate [13,14]. The film was dried in moisture-free air and was irradiated with a ultraviolet light for a given time [8,15,16], the coated substrate was immersed in a 2.5×10^{-4} mol/L ethanol solution of N719 for 24 h to adequately absorb the dye. A flexible TiO_2 film electrode was obtained.

1.3 Assemblage of the flexible DSSC

The flexible DSSC was assembled by injecting the redox electrolyte into the aperture between the TiO_2 porous film electrode (anode) and a Pt-coated ITO/PEN counter electrode. The redox electrolyte is consisted of 0.60 mol/L tetrabutyl ammonium iodide, 0.10 mol/L LiI, 0.10 mol/L I_2, and 0.50 mol/L 4-tert-butyl-pyridine in acetonitrile. The two electrodes were clipped together and a cyanoacrylate adhesive was used as a sealant to prevent the electrolyte leaking. Epoxy resin was used for further sealing the cell to allow measurements to be made.

1.4 Photovoltaic measurements

Photovoltaic testing of the flexible DSSC was carried out by measuring *J-V* curves using an Electrochemical Workstation (CHI660C, Shanghai Chenhua Device Co., China), under irradiation with a simulated solar light from an 100 W Xe arc lamp (XQ-500 W, Shanghai Photoelectricity Device Co., China) in an ambient atmosphere. The incident light intensity was 100 mW cm^{-2} (AM 1.5) and the DSSC active area was 0.8 cm×0.4 cm. Photovoltaic parameters (i.e. fill actor (*ff*), overall energy conversion efficiency (η)) were calculated by the following equations:

$$ff = \frac{P_{\max}}{J_{SC}\times V_{OC}} = \frac{J_{mp}\times V_{mp}}{J_{SC}\times V_{OC}}, \quad (1)$$

$$\eta = \frac{P_{\max}}{P_{in}} = \frac{J_{SC}\times V_{OC}\times ff}{P_{in}}, \quad (2)$$

where J_{sc} was the short-circuit current density (mA cm^{-2}), V_{oc} was the open-circuit voltage (V), P_{in} was the incident light power, and J_{max} (mA cm^{-2}) and V_{max} (V) were the current density and voltage in the *J-V* curves, respectively, at the point of maximum power output.

1.5 Characterization and analysis

A dried powder from the TiO_2 paste was analyzed by X-ray diffraction (XRD) (Cu Kα, Bruker D8 Advance). The

surface morphology of the TiO_2 film was observed with a scanning electron microscope (SEM) (S-4800N, Hitachi, Japan) and a transmission electron microscope (TEM) (H-7650, 80 kV, Hitachi, Japan). The viscosity data of the colloid were collected by a digital viscometer (NDJ-8S, Shanghai, China) at room temperature.

2 Results and discussion

2.1 Effect of stirring time

A highly homogeneous and stable paste plays an important role in the preparation of crack-free TiO_2 films [17]. The influence of stirring time of TiO_2 paste on surface morphology was investigated. The TiO_2 pastes added 6 mol% TTIP was stirred for 0, 24, 48, 72 and 96 h, respectively. The SEM images for the corresponding films were recorded and shown in Figure 1. It can be seen that when stirring time is 24 h, the cracking appear on the TiO_2 film. When stirring time is 48 h, almost no cracks are observed in the film.

Table 1 shows the viscosity of the TiO_2 paste stirred for different times and then hydrothermal treated for 12 h. Without stirring, the viscosity of the system is very small, indicating that the size of TiO_2 conglomeration particle is larger, and surface area is smaller, therefore, cracking occurs easily. Prolonged stirring significantly increases the viscosity of the paste. When the stirring time is 48 h, the viscosity of paste is about 8000 mPa s. This suggests that TiO_2 particles are well dispersed and that the TiO_2 film surface is smooth and crack-free. A paste viscosity of about 8000 mPa s is optimal for preparing films. From the table, stirring for 48 h is an optimal condition, thus following experiments were performed using this stirring time.

2.2 Effect of TTIP

To improve chemical connectivity between TiO_2 particles and its adherence to flexible substrate, we prepared TiO_2 pastes by adding a small amounts of TTIP. Figure 2 shows

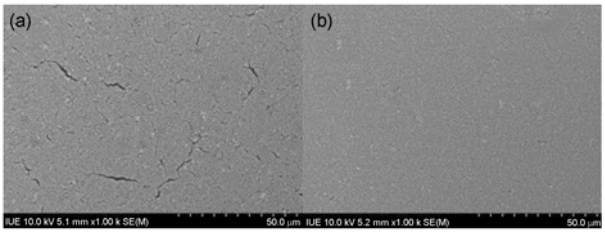

Figure 1 SEM image of the flexible TiO_2 film with the stirring time (a) 24 and (b) 48 h.

Table 1 The viscosity change for the slurry with different stirring time

Stirring time (h)	0	24	48	72	96
Viscosity (mPa s)	238.7	4687.3	7965.6	8055.9	8673.8

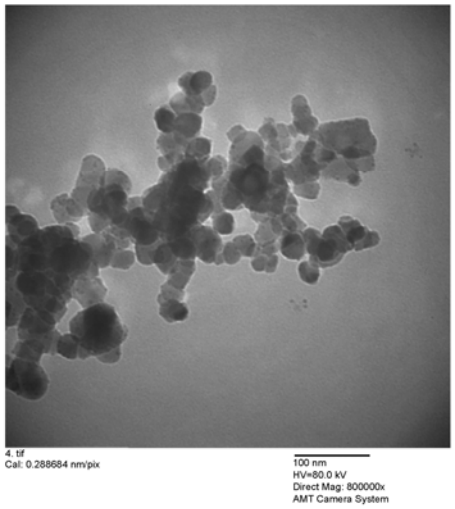

Figure 2 TEM image of a porous nanoparticulate TiO_2 film.

the TEM image of a TiO_2 film with 6% TTIP, it can be seen that the particle diameter of TiO_2 is about 25 nm. And chemical connectivity between TiO_2 particles is improved after adding a small amount of TTIP. Figure 3 shows XRD patterns of TiO_2 powder by adding 0, 2 mol%, 4 mol%, 6 mol%, 8 mol% and 10 mol%, respectively. It can be seen that different TTIP amounts can not change the phase compositions of TiO_2, no other phases of TiO_2 (such as brookite) appear.

To optimize the TTIP content, by using the methods in this paper, the flexible DSSC with TTIP of 0, 2 mol%, 4 mol%, 6 mol%, 8 mol% and 10 mol% were assembled, respectively. Their photovoltaic performances were measured and the results are shown in Table 2.

As shown in Table 2, adding a small amount of TTIP increases the open circuit voltage from 0.721 to 0.76 V, and the fill factor also increase slightly. Short-circuit current density increase with TTIP concentration, and reach a maximum of 7.20 mA cm^{-2} at 6 mol% TTIP. With further increasing the TTIP content, the short-circuit current density

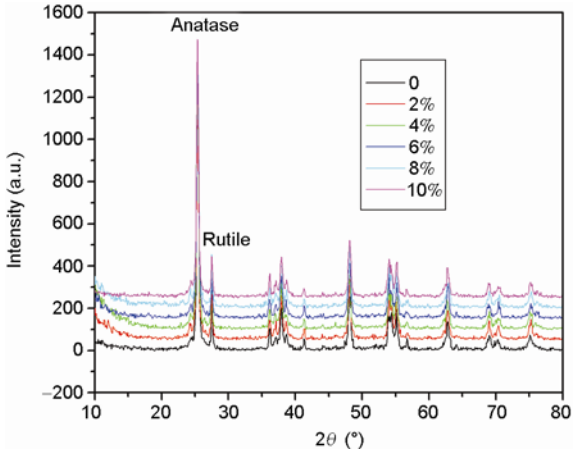

Figure 3 XRD patterns of nanocrystalline TiO_2 particles prepared by adding different mount of TTIP to TiO_2 slurry.

Table 2 Cell performances for adding different amount of TTIP to TiO_2 slurry used for film preparation

TTIP (%)	J_{sc} (mAcm^{-2})	V_{oc} (V)	*FF*	η (%)
0	6.19	0.721	0.641	2.86
2	6.70	0.760	0.655	3.33
4	6.89	0.763	0.669	3.52
6	7.20	0.769	0.686	3.84
8	6.92	0.763	0.681	3.60
10	6.28	0.755	0.644	3.05

decrease. Figure 4(a) shows that at 6 mol.% TTIP, there is very little amorphous solid. In this case, TiO_2 shows a better porosity which favors the adsorptin of dye and higher photocurrent. Connection between TiO_2 particles is also good, which is beneficial for efficient electron transfer, thus high current and a high photoelectric conversion efficiency are observed. Figure 4(b) shows that particle agglomeration is apparent when TTIP content is 10 mol%, which leads to decreased porosity and lower DSSC performance.

2.3 Influence of TiO_2 film UV treatment on DSSC properties

Under usually ambient conditions, the hydrolysis of TTIP is sometimes uncompleted, which may leave residual organic species in the TiO_2 film. Therefore we attempted to further clean the film by UV treatment. Such treatment has been employed for cleaning substrates and/or removing organic contaminants in the synthesis of patterned mesoporous silica films and preparation of self-assembled monolayer [18,19]. Takuroti et al. [20] reported in 2004 that UV-assisted chemical vapor deposition of TTIP onto photoelectrically deposited TiO_2 films drastically enhanced the photocurrent and photovoltage of flexible DSSCs. Table 3 shows performances of flexible DSSCs with TTIP of 6 mol%

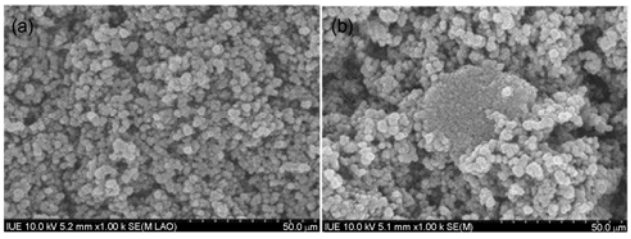

Figure 4 SEM image of the flexible TiO_2 film with molar percentage of (a) 6% and (b) 10%.

Table 3 The photovoltaic performance of DSSCs with different UV treatment time for flexible films

Samples	Time (h)	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	η (%)
A	0	4.85	0.730	0.624	2.21
	1	6.49	0.747	0.671	3.25
	2	7.20	0.769	0.686	3.84
	3	6.44	0.772	0.677	3.59
	4	6.17	0.757	0.661	3.08
B	0	5.23	0.697	0.571	2.08
	2	6.19	0.721	0.641	2.86

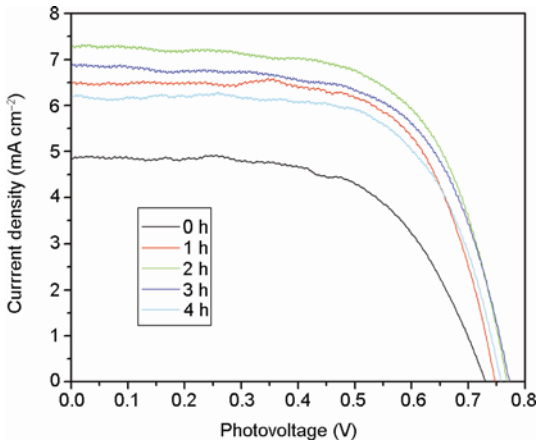

Figure 5 *I-V* curves of dye-sensitized TiO_2 films prepared by the paste with adding the molar percentage of 6% TTIP.

(sample A) and in the absence of TTIP (sample B), with different UV treatment times.

Table 3 and Figure 5 show that with the increasing UV treatment time from 0 to 2 h, open circuit voltage increase slightly, while short-circuit current density, fill factor and overall cell efficiency all increase significantly. The performance of the flexible DSSC reaches a maximum in UV treatment for 2 h. Further increasing treatment time leads to the reduction of short circuit current density, fill factor and efficiency. The UV irradiation can delete a small amount of ethanol, water, and some organic impurities from the TiO_2 film, and the short time UV irradiation does not damage the TiO_2 film or ITO layer of PET [8]. So the photovoltaic performance of the flexible DSSC increase with the increase of UV treatment time less than 2 h. However, when the UV irradiation time is more than 2 h, the destroy of TiO_2 film or ITO layer of PET increases with a increasing UV irradiation time, which leads to a decrease in electron transfer and therefore flexible DSSC performance.

3 Conclusions

In summary, a TiO_2 paste was prepared by mixing commercial TiO_2 (P25), ethanol, distilled water, and a small amount of Ti (IV) tetraisopropoxide (TTIP), following by a hydrothermal treatment. A crack-free flexible TiO_2 film was prepared by scraping the paste on ITO/PEN substrate. Prolonged stirring before hydrothermal treatment can prevent the cracking of TiO_2 films. In our experimental condition, the stirring for 48 h is suitable. TTIP significantly promote the chemical connection between TiO_2 particles and its adherence to the substrate. UV irradiation can remove some impurities and water from the TiO_2 film with an optimal time of 2 h. The resultant flexible DSSC provided a photoelectric conversion efficiency of 3.84% under irradiation with 100 mW cm^{-2} simulated solar light.

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